



## Biomass derived feedstock co-processing with vacuum gas oil for second-generation fuel production in FCC units

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### ABSTRACT

Hydrodeoxygenated pyrolysis-oils (HDO-oil) are considered promising renewable liquid energy carriers. As such, it cannot be applied in in-stationary combustion engines so more “upgrading” is required. A considerable alternative is to co-process HDO-oil along with vacuum gas oil (VGO) in a Fluid Catalytic Cracking unit (FCC). This study evaluates the impact of adding 20 wt.% HDO-oil to a conventional FCC feedstock. The VGO and bio-oil mixtures were co-injected into a fixed-bed reactor simulating FCC conditions using an equilibrated industrial FCC catalyst. Co-processing of 20 wt.% HDO-oil with VGO gave comparable yields for the gasoline fraction to that of the pure VGO cracking. However, during co-processing oxygen removal from HDO-oil oxygenated components consumes hydrogen coming from the hydrocarbon feedstock. As a result the final product composition is poor in hydrogen and contains more coke, aromatics and olefins.

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### 1. Introduction

Due to the depletion of carbon fossil resources (oil, gas and coal) and increased efforts to mitigate CO<sub>2</sub> emissions, new generations of transportation fuels have recently been proposed, involving a partial or complete replacement of fossil resources by carbon-neutral renewable ones. As such, biomass is a promising feedstock since it is abundant and cheap and can be transformed into fuels and chemical products [1,2].

Among the various proposed scenarios, first generation of biofuels, like bio-ethanol and bio-diesel, are now facing environmental and strategic issues, since they are derived from agricultural sources and they are grown in net competition with food production. In that sense, non-competing lignocellulosic biomass sources derived from forestry and industrial wastes are today a preferred feedstock for second generation of transportation fuels [3].

A major challenge to consider is the required mass production given the huge capacities involved in transportation, which means that rapid change can be achieved only by using existing infrastructures and guaranteeing the same quality of final fuels. For that reason, a realistic scenario for biofuels mass production in the short term is to consider “co-processing” of biomass-derived resources

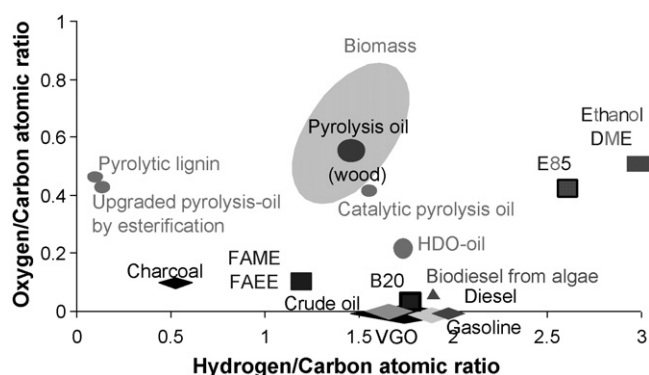
together with conventional crude oil in standard refineries. This co-processing in existing refineries should be economically more competitive than processes such as Fischer–Tropsch fuels obtained from biomass gasification [4] and bio-diesels derived from vegetable oils [5,6].

Within the above context, pyrolysis-oils obtained from lignocellulosic biomass are among the best candidates for co-processing, since the technology for producing them is today validated at a pilot scale [7]. Fast pyrolysis of biomass produces renewable fuels in an environmentally friendly and sustainable way. Pyrolysis-oils are composed of a very complex mixture of oxygenated hydrocarbons (>300) [8], the main constituents being acids, aldehydes, ketones, alcohols, glycols, esters, ethers, phenols and phenol derivatives, as well as carbohydrates and derivatives, and a large proportion (20–30 wt.%) of lignin-derived oligomers [9]. Due to their oxygen rich composition, they present lower heating value, immiscibility with hydrocarbon fuels, chemical instability, high viscosity and corrosiveness [1,10–14]. Therefore the key feature for converting them to fuels by co-processing is to make them compatible with crude oil feedstock, e.g. by lowering their high oxygen content, 30–55 wt.%, depending on the bio-source.

In the last years, a few attempts for directly upgrading the entire pyrolysis-oil without co-processing have been reported for gasoline production by catalytic cracking: significant amounts of tars, chars and coke, and irreversible catalyst deactivation were observed mainly due to the high oxygen content in the feed [15–20]. Thus, the direct feeding of the entire pyrolysis-oil into standard refinery units does not appear as a straightforward task [21].

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**Fig. 1.** Road map for (bio)fuels and feedstocks: van Krevelen diagram adapted from Ref. [28]. First generation biofuels (■), second generation biofuels (●), third generation biofuels (▲), and petroleum based fuels (◆).

Among various upgrading processes, hydrodeoxygenation (HDO) [22] is a promising chemical process to reduce the acidity and oxygen content. HDO is commonly applied using a solid catalyst and hydrogen at elevated temperatures (>600 K) and at high pressures (10–20 MPa). Upon reaction, the oxygen content is reduced considerably, resulting in the formation of water, aliphatic and aromatic components. Co-processing upgraded pyrolysis-oils (HDO type oils) mixed with a hydrocarbon feedstock (vacuum gas oil or straight-run gas oil) in large-scale units, such as Fluid Catalytic Cracking (FCC) or Hydro-Treating (HDT), allows refiners to adjust the content of biocarbon in the produced “hybrid” fuels at a level compatible with international regulations (e.g. EC regulation for 10% by December 2020 on energy content basis of “all petrol and diesel for transport purposes” [23]).

FCC is one of the most important processes of a modern refinery because of its flexibility to changing feedstock and product demands. Its principal aim is to convert high molecular weight hydrocarbons to more valuable products, mainly gasoline [24–27]. The typical FCC catalyst consists of a mixture of an inert matrix, kaolin, an active matrix, alumina, and a binder, silica or silica–alumina and a Y-zeolite [25,27]. These catalysts are efficient at removing oxygen from biomass-derived molecules. Oxygen can be removed as CO, CO<sub>2</sub> or H<sub>2</sub>O through the following simplified reaction pathway:



The change in composition from petroleum to biomass can be illustrated using a diagram developed by Van Krevelen [28]. Fig. 1 shows the changes in the atomic ratios “hydrogen to carbon” and “oxygen to carbon” from biomass-derived fuels to gasoline.

As can be observed from Fig. 1, the “hydrogen to carbon” atomic ratio for vacuum gas oil (VGO) and HDO-oil is comparable but the “hydrogen to carbon” atomic ratio is negligible for the first one and ~0.2 for the last one. The major challenge in biomass conversion is to remove oxygen from the biomass and to increase the hydrogen content of the hydrocarbon products. The oxygen content of the HDO-oil depends on the conditions of the hydrodeoxygenation of the pyrolysis-oil.

Samolada et al. [9] proposed to co-feed a mixture of hydrotreated flash pyrolysis-oil heavy fraction (HBFPL) and light cycle oil (LCO) (15/85, w/w) in a FCC process over a commercial catalyst. The produced bio-gasoline quality is comparable with that of the VGO cracking but with low yields ~20 wt.%. Lappas et al. [29] continued this study by blending the above HBFPL/LCO mixture with a conventional FCC feed (VGO) (2.25/12.75/85) and co-feeding it into an FCC unit. The obtained gasoline quality was compared to the VGO/LCO (85/15, w/w) feed, the presence of HBFPL resulted in higher aromatics content and less paraffins and olefins.

**Table 1**

VGO and HDO-oil composition by simulated distillation.

Mass recovery (wt.%)	Boiling point range (°C)	
	VGO	HDO-oil
Initial	151	36
5	212	76
10	253	99
30	329	211
50	373	308
70	422	405
90	492	517
Final	578	594

In the present work, we investigate how co-feeding HDO-oil with VGO in a fixed-bed reactor can influence the product distribution and the product quality.

## 2. Experimental

### 2.1. Materials

An equilibrated industrial FCC catalyst containing ~15 wt.% Y-zeolite was used.

The vacuum gas oil has been characterized by simulated distillation and its boiling point distribution is given in Table 1. Its elemental composition is given in Table 2. Pyrolysis-oil was obtained by flash pyrolysis of forest residue (pine wood). The HDO-oil was prepared at the University of Twente (The Netherlands) from the filtered bottom phase fraction of the pyrolysis-oil. This fraction was hydrogenated at 290 bar and 330 °C over a carbon supported ruthenium catalyst. The HDO-oil has been characterized by simulated distillation and its boiling point distribution is given in Table 1. The density and elemental composition of the final HDO-oil are shown in Table 2. Preliminary experiments were performed to check the miscibility of different pyrolysis-oils with VGO. Pyrolysis-oils having less than 20 wt.% of oxygen content mix well with VGO giving a homogeneous mixture that can be handled with a HPLC pump.

### 2.2. Set-up

Experiments were performed in a fixed-bed quartz reactor (ID = 12 mm, L = 340 mm) containing 1.0 g of catalyst at 1.2 bar. The equipment has already been validated with respect to a microactivity test reactor (MAT) for VGO cracking [30]. A thermocouple was located inside the catalyst bed. Argon was used as a carrier gas (flow = 100 ml/min). One reaction cycle consists of 1 min cracking at 500 °C, 18 min of stripping under argon flow at 500 °C, 40 min regeneration under 20 vol.% of O<sub>2</sub> in Ar at 650 °C and 11 min purge. The liquid feed was varied to obtain different catalyst to oil ratios. During the cracking and stripping steps, the liquid product was collected in a glass receiver located at the exit of the reactor and kept at –50 °C. Meanwhile, the gases were collected in a gasbag. The amount of coke formed on the catalyst was estimated from

**Table 2**

Properties of VGO and HDO-oil.

Properties	VGO	HDO-oil
Density (g/cm <sup>3</sup> at 25 °C)	0.8953	0.9323
Sulfur (wt.%)	2.02	–
Nitrogen (wt.%)	0.07	–
Hydrogen (wt.%)	12.4	10
Carbon (wt.%)	85.4	69
Oxygen (wt.%)	–	21
Conradson C (wt.%)	0.26	–

the carbon dioxide production during the regeneration period, as measured by mass spectrometry.

Cracking was performed at three different carbon to oil ratios (referred to as C/O): 2.9, 4.5 and 5.9 corresponding to weight hourly space velocities (WHSV) of  $20\text{ h}^{-1}$ ,  $13\text{ h}^{-1}$  and  $10\text{ h}^{-1}$ , respectively. The C/O ratios were varied by changing the amount of feed injected into the reactor, but by keeping the amount of catalyst constant.

### 2.3. Analysis

The gases during cracking/stripping cycles were analyzed using an Agilent 3000A micro-gas chromatograph equipped with three columns (molecular sieve 5A ( $10\text{ m} \times 0.32\text{ mm}$ ), PorapLOT-U ( $8\text{ m} \times 0.32\text{ mm}$ ), OV-1 ( $8\text{ m} \times 0.15\text{ mm} \times 2\text{ }\mu\text{m}$ )) and a thermal conductivity detector for  $\text{H}_2$ , C1–C6 hydrocarbons. As an internal standard He was used. Gaseous products obtained during regeneration cycles were analyzed on-line by a mass spectrometer (VG-Prolab with a closed ion source). This mass spectrometer (MS) was regularly calibrated for CO and  $\text{CO}_2$  and He was used as an internal standard. The errors in the coke yields are estimated as less than  $\pm 5\%$ .

Liquid samples were analyzed on a HP6890 gas chromatograph equipped with an ASTM-2887 system and analyzed according to their boiling point range.

For more chemical information, liquid samples were also analyzed by a GC  $\times$  GC system. It consists of a modified 6890N gas chromatograph (Agilent) equipped with a two stages thermal modulator (Zoex Corporation) and low temperature valve controlling a cold jet ( $-100^\circ\text{C} < T < -120^\circ\text{C}$ , using liquid nitrogen) to provide narrow pulses. A short thermal desorption at  $280^\circ\text{C}$  releases the trapped solutes and injects them into the second column. The secondary column effluent was analyzed using a mass selective detector 5975B (Agilent). In this work, only the total response of the MS detector is used as an indication of the evolution of specific compounds; thus providing a semi-quantitative analysis.

For every experiment it is possible to assess the yield of individual hydrocarbons or groups, and the following main groups were defined: dry gas ( $\text{H}_2$ , CO,  $\text{CO}_2$ , C1–C2 hydrocarbons), liquefied petroleum gas (LPG: C3–C4 hydrocarbons) gasoline (C5:  $221^\circ\text{C}$  boiling point), light cycle oil (LCO:  $221\text{--}370^\circ\text{C}$  boiling point), bottom fraction (boiling point  $> 370^\circ\text{C}$ ) and coke. The conversion is defined as a sum of the yields of dry gas, LPG, gasoline and coke. Mass balances in all the experiments are closed to 95%. The yield of each fraction is given by

$$\text{Yield of fraction } i (\%) = \frac{\text{mass of fraction } i}{\text{total mass in the feed}} \times 100 \quad (2)$$

The water content in the liquid effluent was measured by the Karl–Fischer method. Oxygen content in the liquid effluent was determined by elemental analysis.

### 3. Results

To simulate co-processing in a FCC unit, a mixture of VGO with 20 wt.% HDO-oil and pure VGO were processed in a fixed-bed reactor. As seen in Fig. 2 three cracking sequences were run over the equilibrated FCC catalyst:

- (i) pure VGO cracking,
- (ii) VGO/HDO-oil co-processing, and
- (iii) again pure VGO cracking.

The third sequence (iii) was run in order to determine the effect of co-processing on the catalyst activity. As very little data are available on co-processing of HDO-oil, it is interesting to study the effect of the renewable feedstock on the catalyst stability. The

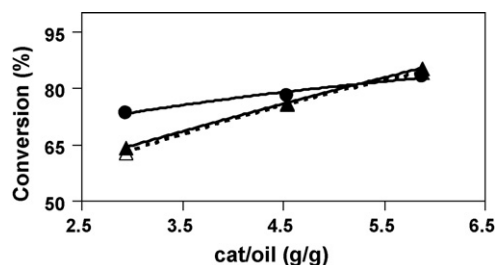


Fig. 2. Influence of different C/O ratios on the feed conversion. VGO cracking ( $\Delta$ ), mixture of VGO with 20 wt.% HDO-oil co-processing ( $\bullet$ ) and VGO cracking after co-processing ( $\nabla$ ).

product distributions for sequences (i) and (iii) have not changed significantly (within the experimental error), indicating negligible catalyst alteration during one cycle of co-processing. Even the apparent increase in hydrogen production as shown in Fig. 4 amounts to less than 0.1 wt.%, well within the experimental error.

The study was performed at three different C/O ratios: 2.9, 4.5 and 5.9 so as to observe the co-processing effect at different conversion levels. The C/O ratio includes the weight of both HDO-oil and VGO in calculating the feed weight.

The conversion increases with the C/O ratio, for both pure VGO cracking as for co-processing although in the latter case the increase with the C/O ratio is less pronounced. At a low C/O ratio of 2.9, co-processing gives higher conversion values than the pure VGO cracking, while at higher C/O ratios of 5.9 the conversions are similar. The higher co-processing conversion at C/O = 2.9 might in a part be due to the fact that the HDO-oil already contains molecules in the product range.

Co-feeding HDO-oil induces changes in the product distribution. Fig. 3 shows a comparison of the coke yields for the VGO and the VGO/HDO-oil mixture at the same value of the C/O ratio, but at different conversions. The coke formation tendency is much higher for co-processing compared to cracking. At 80% conversion the coke amount is two units higher for co-processing than for cracking.

HDO-oil addition to the VGO has various effects on the cracking product distribution. As shown in Fig. 3 cracking of the mixture produces higher yields for dry gas, lower for LPG while the yields of gasoline, LCO and bottom are comparable to those corresponding to the cracking of VGO.

The high production of low-value dry gas during co-processing relates to the HDO-oil thermal cracking forming more ethane and methane compared to VGO cracking and also because of the  $\text{CO}_2$  (Fig. 4) formation from oxygenates decomposition. The desired product is gasoline but LPG and LCO are also considered as valuable products, being feedstock for diesel production. LPG production is lower for the mixed feed, which can be due to the fact that it contains more aromatic components that are difficult to crack than the pure petroleum feedstock. LCO yields are increasing with the conversion and are similar for both types of feed, within the experimental error (Fig. 3). This range is not affected by the co-processing. The bottom fraction is associated with the non-converted fraction and the primary cracking of the heavy hydrocarbons. Bottom yields are slightly lower for VGO/HDO-oil. The high molecular weight compounds in HDO-oil have a higher tendency for coke formation and thus no longer contribute to the bottom fraction, which decreases.

The yields of the different gas-phase products do change with the feedstock as shown in Fig. 4. Compared to VGO, VGO/HDO-oil cracking products formation rates follow similar trends for  $\text{H}_2$ ,  $\text{CH}_4$ , C2's, C3's, C4's. The yields for  $\text{CH}_4$ , C2's, C3's and  $\text{CO}_2$  during co-processing increase rapidly with increasing conversion. CO production is low for both feeds,  $\sim 0.05\text{ wt.}\%$ .

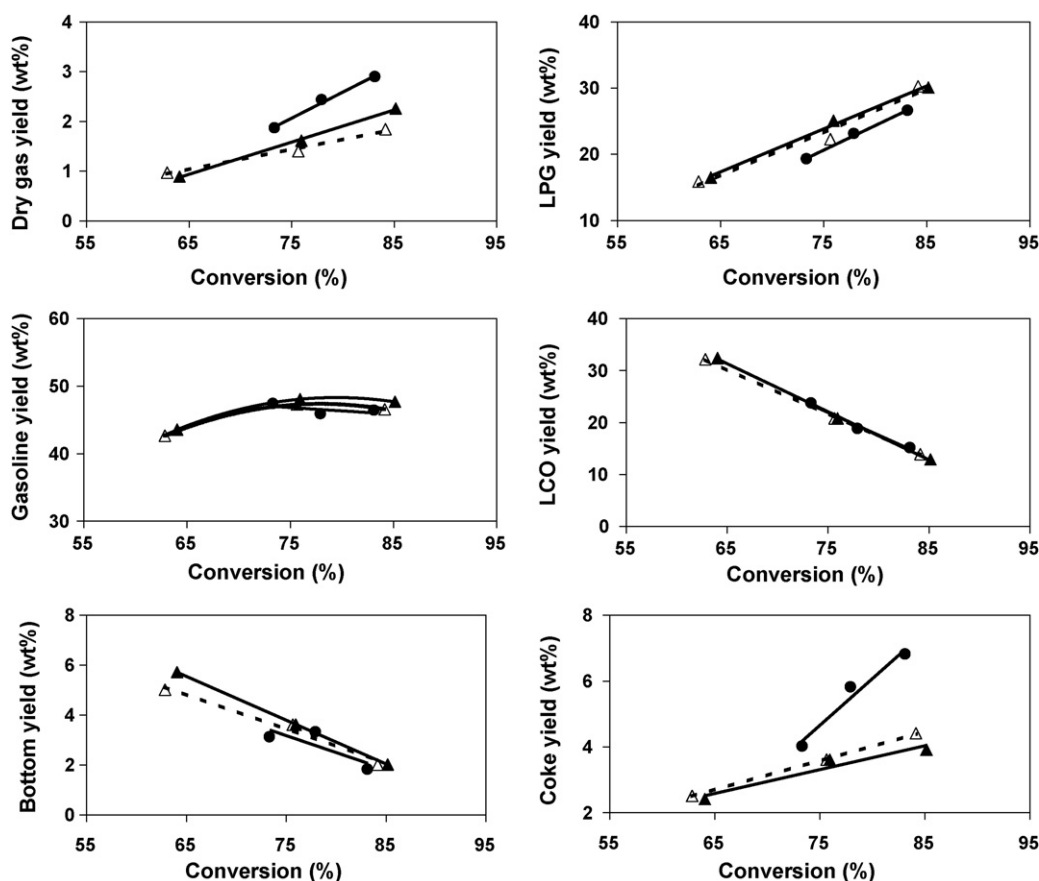


Fig. 3. Effect of the feed on the yields at different conversion levels. VGO cracking (▲), VGO/HDO-oil co-processing (●) and VGO cracking after co-processing (△)

CO<sub>2</sub> formation is negligible during VGO cracking since it contains no oxygen. On the other hand, during co-processing the feed already contains 4 wt.% oxygen, thus CO<sub>2</sub> forms according to Eq. (1). This rate increases rapidly with the conversion as a function of the oxygenated compound decomposition. Similar trends are observed for the production of water (Table 3). Methane, C2 and C3 formation increases faster with the conversion during co-processing than during VGO cracking. The C4 formation is slightly lower during VGO/HDO-oil co-processing than during pure VGO cracking.

The gasoline fraction is the primary objective of a FCC unit. So it is of importance to see the impact of the HDO-oil for this product range. Gasoline yields are similar for VGO/HDO-oil co-processing and for pure VGO cracking (Fig. 3).

The overall cracking product distribution of the liquid phase, i.e. gasoline, LCO, and bottom fraction, based on the boiling point distribution does not give a lot of information on the chemical composition. To get a better picture, a more detailed analysis was performed by GC × GC on the volatile part of the liquid phase (Fig. 5). This technique has already been used for the HDO-oil prod-

uct identification and classification [8]. The volatile part of the liquid phase corresponds to the product fraction that can be analyzed by the GC × GC technique, which corresponds to molecules with a molecular weight of less than 800 g/mol.

The cracking products are classified into the following families: aliphatics, mono-, di-, tri- and tetraaromatics (Fig. 6). As observed for both feeds, aliphatic yields and all the aromatics are decreasing with the increase of the conversion. Aliphatic and monoaromatic yields are slightly higher for VGO/HDO-oil. Di-, tri- and tetraaromatic yields are the same for both types of feed. At high conversion there are no more tetraaromatic compounds left among the products (for VGO this is at 82% and for VGO/HDO-oil at 86% conversion).

### 3.1. Gasoline range product distribution

The GC × GC technique was used to explore in more detail the gasoline fraction as simulated distillation technique gave similar yields for the gasoline fraction for either VGO cracking or VGO/HDO-oil cracking. At ~73% conversion, gasoline yields are similar for both types of feeds. It is interesting to see whether the compositions of the produced gasoline are similar as well. All the compounds are grouped in the following families: aliphatics, mono-, and diaromatics. The product distribution within the gasoline range is shown at three different conversion levels in Fig. 7. As observed for both feeds, aliphatic, mono-, and diaromatics formation decreases with the increase of the conversion.

Paraffins, naphthenes and alkylbenzenes are identified in the GC × GC chromatogram as the major products of the gasoline fraction. Straight and branched paraffins were identified in the C7–C13 range corresponding to a commercial gasoline composition [31]. The main naphthene constituents consist of cycloalkanes with five-

Table 3  
Oxygen balance during co-processing at a given conversion.

C/O ratio	O content (mmol)	
	2.9 (Conv.: 73%)	4.5 (Conv.: 78%)
Initial	0.52	0.34
CO <sub>2</sub>	0.07	0.084
CO	0.0005	0.0005
H <sub>2</sub> O	0.134	0.032
Residual oxygenated	0.109	0.052
Not classified	0.2065	0.1715



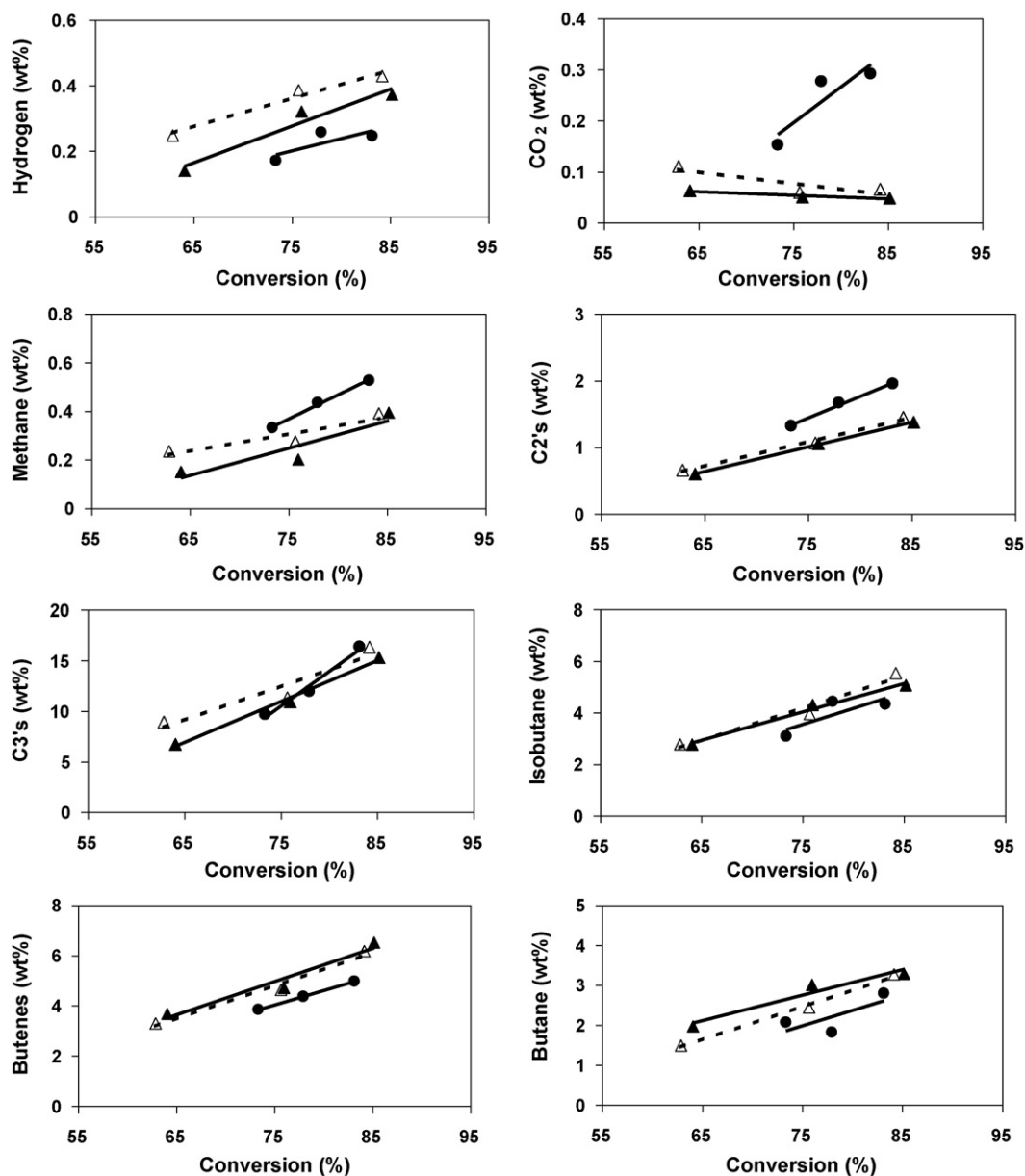


Fig. 4. Gas-phase yields at different conversion levels. VGO cracking (▲), VGO/HDO-oil co-processing (●) and VGO cracking after co-processing (△)

or six-member rings with alkyl-chains up to C5. The alkylbenzene constituents consist mainly of methyl-, ethyl- and propylbenzene, benzene and toluene.

The detailed compositions of the gasoline at a given conversion (~85%) are compared in Fig. 8 for VGO and VGO/HDO-oil. Co-processing favors more branched paraffin formation at the expense of linear paraffins compared to VGO cracking. Short alkyl-chain (C1–C3) benzene derivatives are more typical for the VGO/HDO feed than for the pure VGO cracking.

### 3.2. Oxygen balance

The HDO-oil contains typical oxygenated compounds such as acids (~7 wt.%), aldehydes (4–10 wt.%), furans (<1 wt.%), guaia-cols, syringols (1–4 wt.%), alkylphenols (9–15 wt.%), alkylbenzenes (24–30 wt.%), and hydrocarbons (3–10 wt.%) [8]. The HDO-oil used here contains ~21 wt.% oxygen so it is of interest to establish an oxygen balance based on the following oxygen containing compounds: oxygenated molecules, CO<sub>2</sub>, H<sub>2</sub>O, CO and components that have not

been classified (Table 3). The global oxygen content of the total liquid fraction after reaction was based on elemental analysis. Water is produced by dehydration reactions [32] as well as by catalytic aldol-condensation [33].

During VGO/HDO-oil co-processing CO<sub>2</sub> formation increases with the conversion (Table 3), indicating the decrease of oxygenated compounds. Even at a VGO/HDO-oil conversion level of 86%, some oxygenated compounds remain. Alkylphenols are initially present in high concentrations in the HDO-oil and their deoxygenation is slower than other oxygenated components such as aldehydes [8]. Detailed analyses of the products by GC × GC analysis confirmed the presence of non-converted alkylphenols (Fig. 9) among the co-processing products. The presence of phenol and alkylphenols with side chains up to C5 was observed.

The decomposition of alkylphenols as a function of the conversion is shown in Fig. 10. Phenol and alkylphenols with up to C2 side chains were identified among the co-processing products. C3, C4 and C5 side chain-containing phenol transformation is complete at 71% conversion. The concentration of C2 and C1 alkylphenols

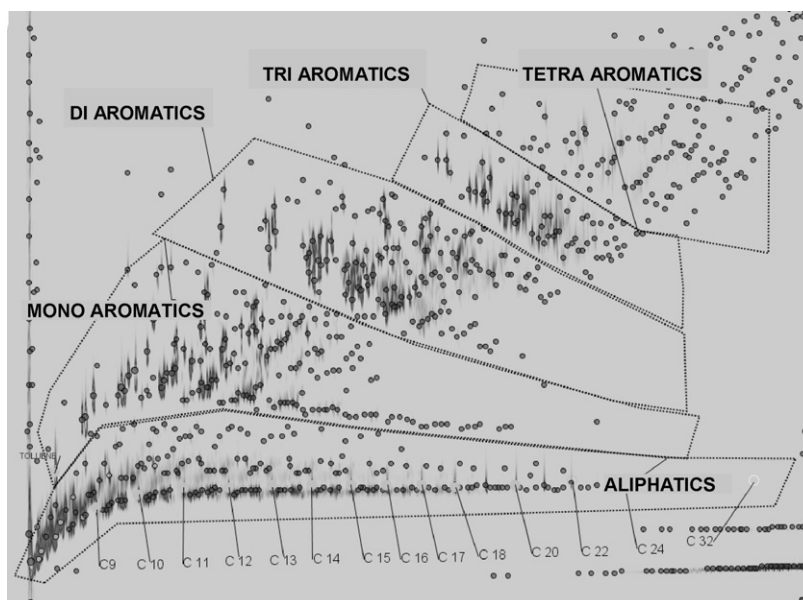


Fig. 5. Contour plot of volatile part of the liquid phase products from VGO/HDO-oil cracking.

decreases much slower, i.e. at 86% conversion still ~30% of the initial C1 alkylphenols can be found. Phenol formation increases at low conversion compared to its initial concentration and only at a higher conversion does it start to decrease. At 500 °C dealkylation and dehydroxylation are considered to be the most important reactions. Dealkylation leads to C1 and C2 alkylphenols and phenol, dehydroxylation to benzene and alkylbenzenes.

#### 4. Discussion

##### 4.1. Impact of co-processing on reaction pathways

The chemical reactions that occur in a FCC process are a large network of many reactions; a simplified scheme of hydrocarbons cracking over acid catalysts is shown in Scheme 1.

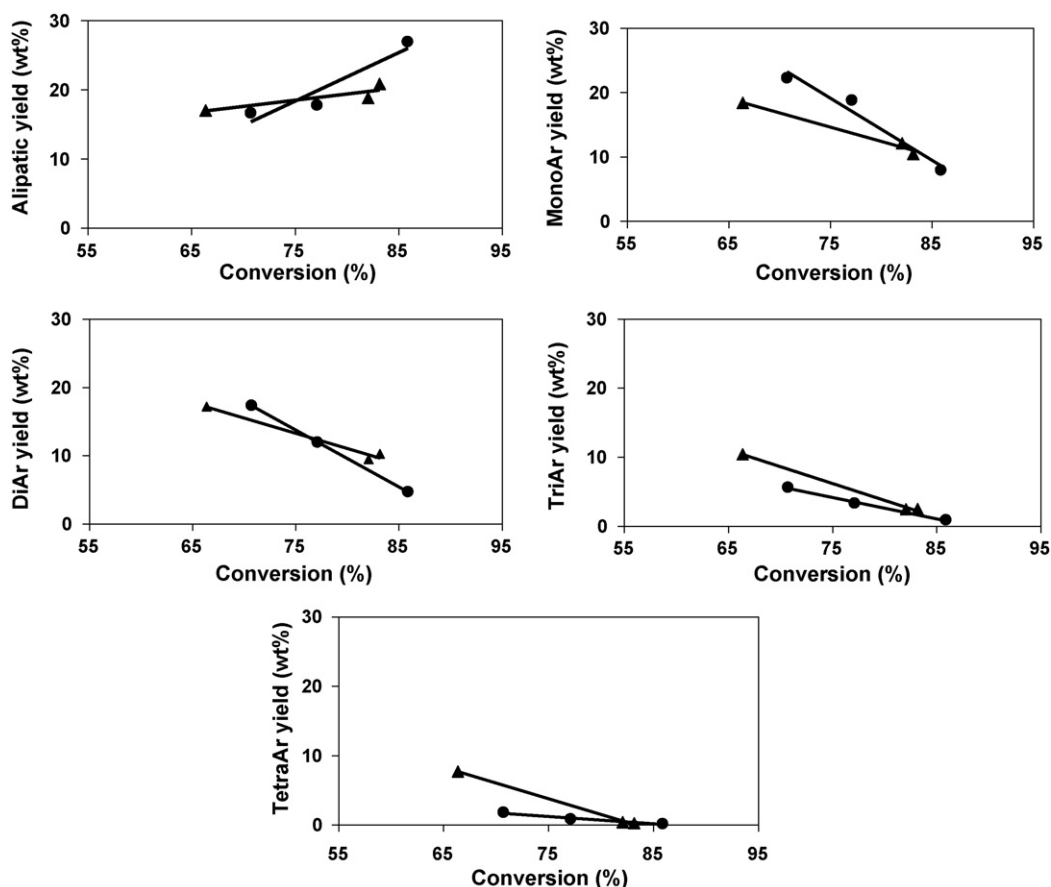


Fig. 6. Liquid-phase composition by GC × GC at different conversion levels on the total liquid product. VGO cracking (▲) and VGO/HDO-oil co-processing (●).

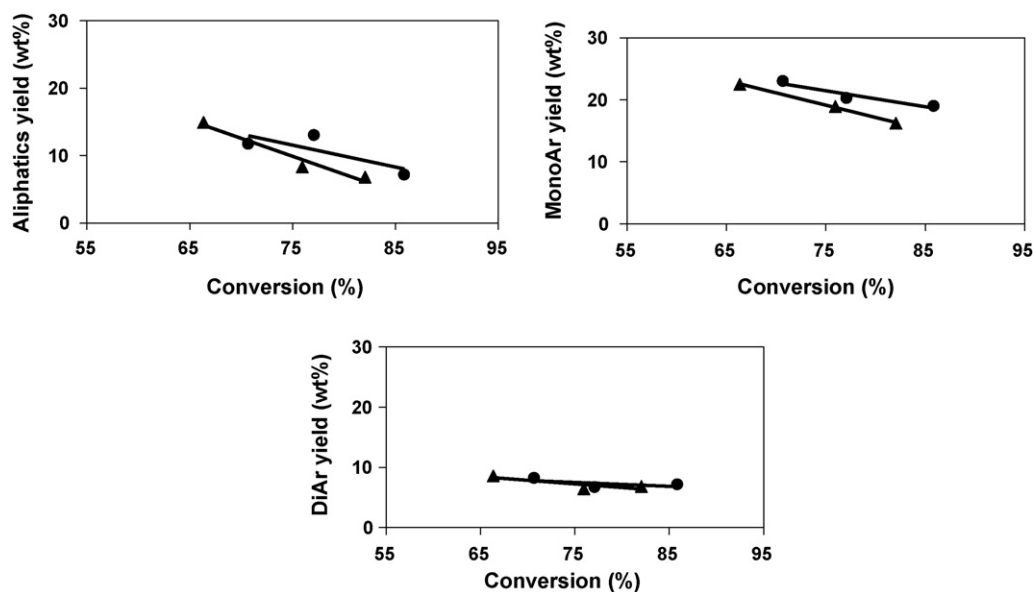


Fig. 7. Gasoline range by GC × GC at different conversion levels for VGO cracking (▲) and VGO/HDO-oil co-processing (●).

Cracking of hydrocarbons over a FCC catalyst leads to smaller hydrocarbons and coke as a result of the following reactions: (1) cracking, (2) hydrogen producing reactions, (3) hydrogen-consuming reactions, and (4) production of larger molecules by C–C bond formation such as Diels–Alder reactions.

Cracking of HDO-oil oxygenates over an acid catalyst in addition to hydrocarbons and coke formation also yields smaller oxygenated molecules, CO<sub>2</sub>, H<sub>2</sub>O, and CO.

Corma et al. extended the above scheme to the cracking of oxygenated molecules by including step (5) dehydration (Scheme 2) [2].

Oxygenated hydrocarbons decomposition starts by breaking of the C–C and C–O bonds by  $\beta$ -scission. Over an acid catalyst C–C and C–O bond cleavages are competing. Decarboxylation and decarbonylation reactions proceed more rapidly than C–C bond cleavage in saturated hydrocarbons [34]. These reactions finally yield CO, CO<sub>2</sub> as the main oxygenated compounds and a mixture of hydrocarbons produced by different reactions such as  $\beta$ -scission, hydrogen

transfer, isomerization, cyclization or aromatization. On the other hand for the unsaturated hydrocarbons in the HDO-oil, the C–C cleavage will take place before the breaking of the C–O bonds of the oxygenated compounds. Therefore they are not completely converted into CO, CO<sub>2</sub> and end up in the final product as smaller oxygenated compounds or as coke.

Furthermore HDO-oil oxygenates conversion occurs mainly via hydrogen-consuming reactions, besides some minor hydrogen producing reactions (Scheme 2). Two main hydrogen-consuming reactions are water formation and hydrogenation reactions and the only hydrogen supply comes from the hydrocarbon feed. The yield of hydrogen produced from VGO/HDO-oil cracking was lower (Fig. 4) than that of the pure VGO cracking, indicating either that the H<sub>2</sub> was consumed in synergetic reaction or that H<sub>2</sub> production was inhibited. This last suggestion is less probable as the initial VGO/HDO-oil feed contains already less H<sub>2</sub>. The result of using VGO/HDO-oil feedstock is that the products are rich in unsaturated hydrocarbons. Moreover, the hydrogen elimination from hydrocarbons produces a higher yield of aromatic compounds. If hydrogen elimination continues from the aromatic compounds polyaromatic components are formed enhancing the coke formation. Besides coke formation through a catalytic route, part of the coke comes from the thermal process through free radical formation which are not able to enter into the catalyst pores and are deposited in the most external part of it for both type of feeds [35]. Further coke deposition is possible with the mixed VGO/HDO-oil feed because of the primary heavy oxygenated hydrocarbons (lignin derivatives) presence. A number of studies dealing with the cracking of pure oxygenated model compounds [19,20] as well as cracking of pyrolysis-oil [16,17] report the formation of large amounts of coke. Adjaye et al. [9,19] attributed this to the polar nature of the oxygenated compounds that results in a stronger adsorption on the acid sites where the coke precursors are formed. During VGO/HDO-oil co-processing larger amounts of coke are produced. The coke might (partially) block the acid sites or cause pore blocking. This results in a decrease of the acid site concentration and in a stronger diffusion limitation inside the pores [36–40].

Besides the presence of the oxygenated compounds among the products, co-processing induces changes in the hydrocarbon product distribution as well. Ethylene represents ~35 wt.% of the dry gas

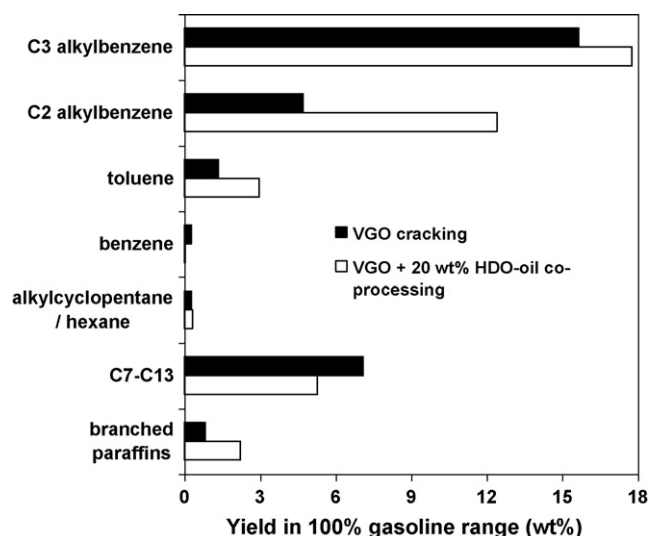


Fig. 8. Detailed gasoline range composition by compounds at ~85% conversion level.

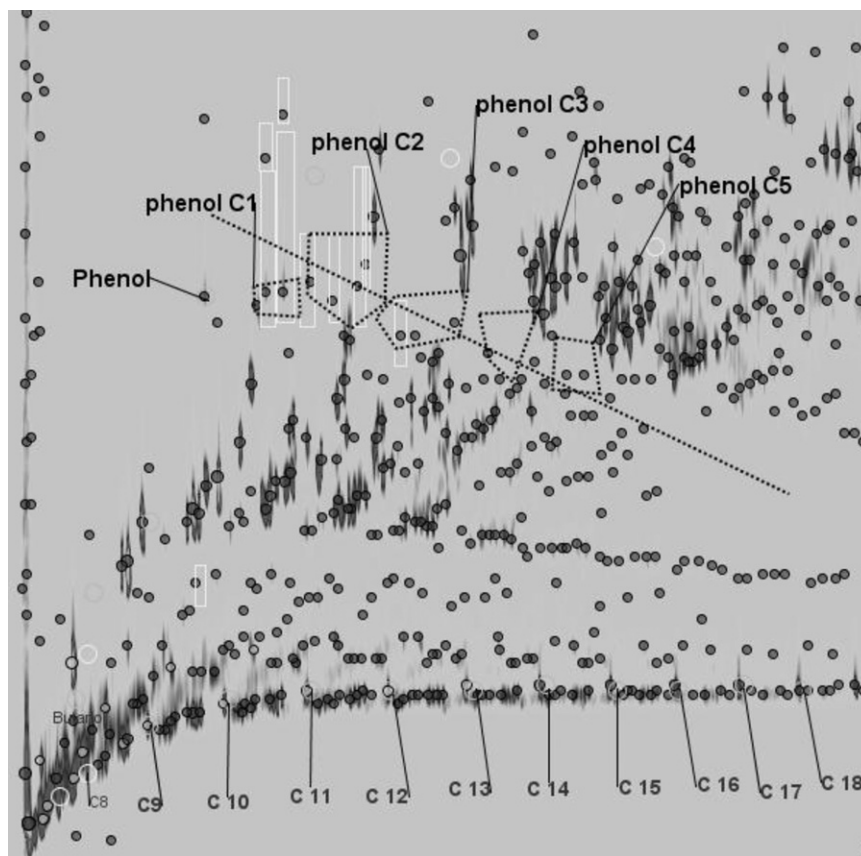


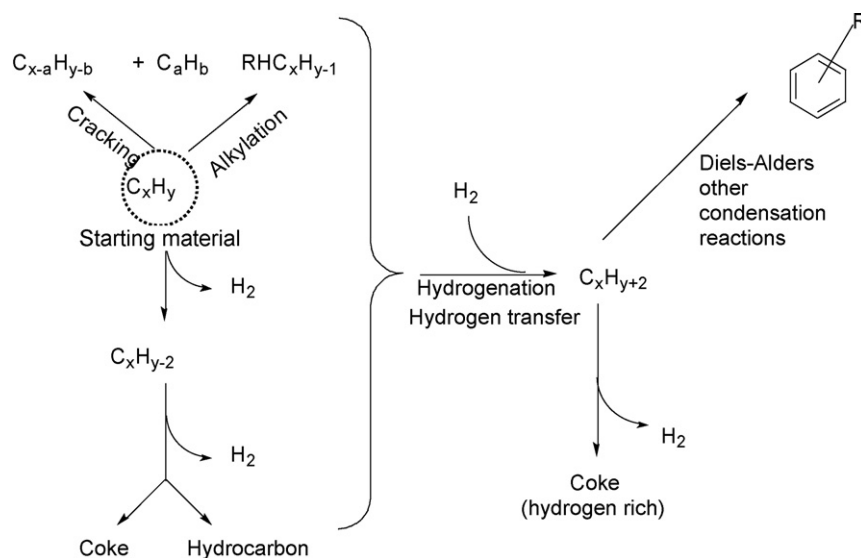
Fig. 9. Zoom on the alkylphenols.

composition for VGO cracking and its content increases to 45 wt.% during co-processing. Methane and ethane formation are higher for co-processing suggesting that more thermal cracking occurs in the HDO-oil than in the hydrocarbons.

Propylene represents ~40% of the total LPG composition. Isobutane formation is also important. In smaller amounts, the isomers of the C4 olefins are produced with a ratio of 1 (C4= to iC4=). C3

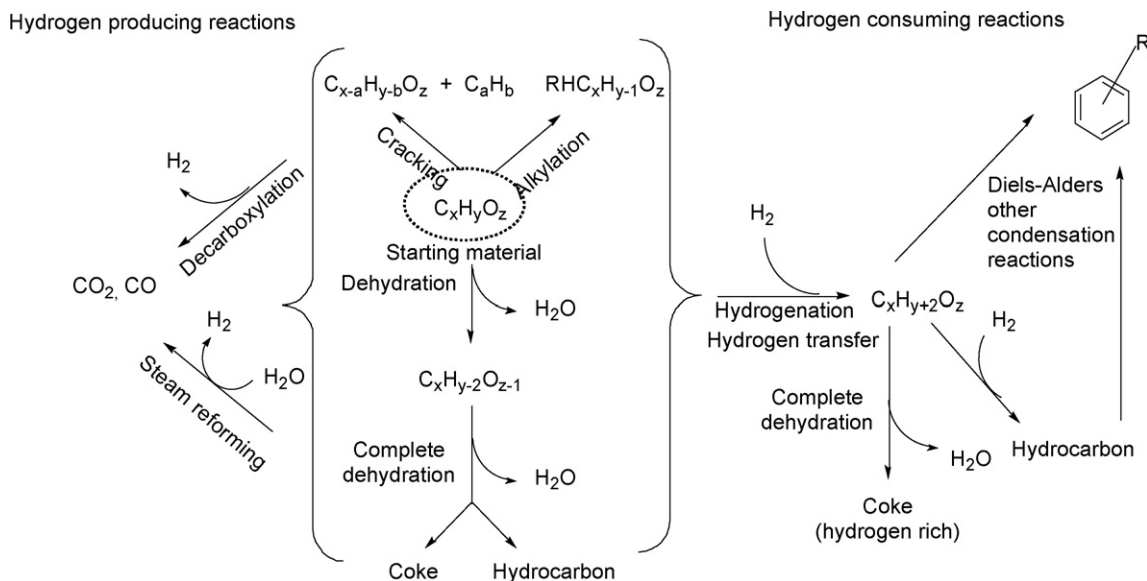
and C4 olefins are stable as they are not able to undergo  $\beta$ -scission reactions [35].

Co-processing results in a higher amounts of aromatic compounds in the gasoline, HCO, LCO and bottom ranges as the mixed feed initially already contains more aromatic compounds than the pure feed. Aromatics are more refractory to cracking than a paraffinic feedstock because of the low H-content [41].



Scheme 1. Catalytic cracking of hydrocarbons over acid catalysts.





Scheme 2. Reaction pathways for the catalytic cracking of HDO-oil oxygenates.

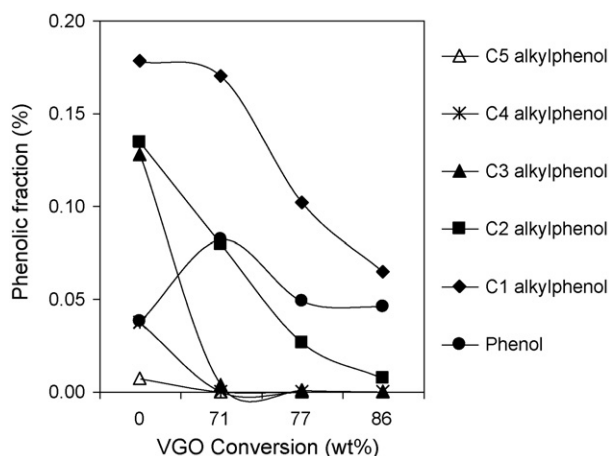


Fig. 10. Alkylphenol conversion during co-processing at different C/O ratios over a FCC catalyst.

## 5. Conclusions

A mixture of 80 wt.% VGO with 20 wt.% hydrodeoxygenated pyrolysis-oil was processed in a fixed-bed reactor simulating FCC conditions and compared to the processing of pure VGO. During co-processing under FCC conditions most of the oxygen is removed in the form of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  by means of decarboxylation and dehydration reactions.

Cracking of the mixture produces higher dry gas yields and coke, lower LPG yields while gasoline and LCO yields are comparable to those of the cracking of VGO. Bottom fraction yields are slightly lower for VGO/HDO-oil co-processing than VGO processing.

Gasoline yields are similar for VGO/HDO-oil co-processing and for pure VGO cracking. Over the equilibrated FCC catalyst ~75% hydrocarbon conversion of the VGO/HDO-oil give comparable results to that of the pure VGO cracking. However during co-processing oxygen removal from HDO-oil oxygenates consumes hydrogen coming from hydrocarbon cracking. As a result, the final product composition is poor in hydrogen and contains more coke, aromatics and olefins. Moreover, the phenolic fraction was not converted completely.

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